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Photochemical Consequences of Interchromophoric Interactions

Final Report

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Final Report

1. Problem: Statement and Summary

This project has been concerned with the photochemical and photophysical consequences of interaction between two or more nonconjugated functional groups upon electronic excitation, i.e.

$$A-0-B \xrightarrow{hv}$$
?

During the period of time encompossed by this grant, we have specifically examined nonconjugated aryl-olefins and aryl-chlorides. The former results have been summarized in a review: "Photochemistry of Organic Bichromophoric Molecules", Acc. Chem. Res., 12, 383 (1979). The latter were published in preliminary form in J. Am. Chem. Soc., 102, 372 (1980).

In sum, we have shown that (1) there are a number of ways in which one functionality in a molecule can interact with the excited state of a second group (2) among these are activation and reactivity of the group <u>not</u> initially excited by the incident light as well as deactivation of the absorber and (3) some of the modes of interaction so far uncovered are subject to appreciable stereoelectronic restrictions.

In addition to the above, we have uncovered a new indene phototransposition reaction, the details of which have been communicated (cf. J. Am. Chem. Soc., 99, 3507 (1977) and J. Am. Chem. Soc., 100, 7109 (1978)).

2. Technical Reports

- 1. to 6/30/76
- 4. to 12/31/77
- 7. to 12/31/79

- 2. to 12/31/76
- 5. to 6/30/78
- 3. to 6/30/77
- 6. to 6/30/79

3. Publications

Xenon Perturbation as a Mechanistic Probe in Solution Phase Photochemistry, H. Morrison, T. Nylund and F. Palensky, J. Chem. Soc. Chem. Comm., 4 (1976).

Photolysis of 2-Methylenebenznorbornene in Protic Media. A Novel Photoinduced Anti-Markovnikov Addition to the Double Bond, H. Morrison and T. Nylund, J. Chem. Soc. Chem. Comm., 785 (1976).

Photochemically Induced Skeletal Rearrangement of Alkyl Substituted Indenes, F. J. Palensky and H. Morrison, J. Am. Chem. Soc., 99, 6353 (1977).

Photosensitized Anti-Markovnikov Addition of Methanol to Homoconjugated Aryl-Olefins, D. D. Neidigk and H. Morrison, J.C.S. Chem. Comm., 600 (1978).

Carbene Photocycloelimination from a Vinyl-Cyclopropane, M. Pallmer and H. Morrison, J.C.S. Chem. Comm., 558 (1978).

Photochemistry of Bichromophoric Molecules. Photochemistry and Photophysics of 2-Methylenebenznorbornene and Related Non-Conjugated Aryl-Olefins in Non-Protic Media, F. Scully, T. Nylund, F. Palensky and H. Morrison, J. Am. Chem. Soc., 100, 7352 (1978).

Photochemistry of Bichromophoric Molecules. Photochemistry and Photophysics of 2-Methylenebenznorbornene and Related Molecules in Protic Media, T. Nylund and H. Morrison, J. A. Chem. Soc., 100, 7364 (1978).

Stereochemistry of the Indene Phototransposition Reaction and the Mechanistic Implications Thereof, D. Giacherio and H. Morrison, J. Am. Chem. Soc., 100, 7109 (1978).

Photochemistry of Organic Bichromophoric Molecules, H. Morrison, Acc. Chem. Res., 12, 383 (1979).

Intramolecular Aryl-Assisted Photolytic Cleavage of 2-Benzonorbornenyl Derivatives. A High Excited State Exo/Endo Reactivity Ratio and a Novel Wagner-Meerwein Rearrangement, H. Morrison and A. Miller, J. Am. Chem. Soc., 102, 372 (1980).

Photochemistry of Bichromophoric Molecules. Intramolecular Excited-State Interactions in the <u>cis</u> and <u>trans</u> Decalin Connected Aryl-Olefins: 7-Methylene-13 β -methyl-5,6,7,8,9,10,13 β ,14 β (and 14 α)octahydrophenanthrenes, M. Pallmer and H. Morrison, J. Org. Chem., 45, 798 (1980).

4. Scientific Personnel

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